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Effect of temperature and pressure on a water-benzene mixture as studied
by infrared spectroscopy

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Abstract

A water-benzene mixture has been studied by infrared spectroscopy at temperatures and pressures in the 473-648 K and 100-350 bar ranges. The OH stretching band intensity has been obtained as a measure of water concentration in the mixture. In the temperature range of 473-523 K, the intensity is almost independent of pressure. On the contrary, at higher temperatures, the absorption intensities exhibit remarkable pressure dependence. Moreover, the intensities increase with increasing temperature toward a certain temperature and then steeply decrease at higher temperatures. It has been found that the turning points of the intensities are located on an extended line of the liquid-liquid-gas three-phase equilibrium curve of the water-benzene mixture and near the critical curve between the two-phase and one-phase regions. This fact suggests that density of the mixture changes steeply across those lines. We have also observed coalescence of two bands, which are assigned to hydrogen-bonded and hydrogen-bond-free OH, respectively, at the higher temperatures and discussed rotational motion of a water molecule in a hydrogen-bonded cluster.

1. Introduction

A weak interaction between water and hydrocarbons is important to understand structure of biological compounds such as proteins and peptides in solutions. However, hydrocarbons are almost immiscible or only poorly miscible with water, being described as hydrophobic, and the experimental data available are limited to very dilute solutions. To study the water-hydrocarbon interaction from a molecular viewpoint, it is desirable to examine a wide range of concentration. This can be performed by high-temperature-pressure experiments. Water and hydrocarbons become significantly miscible with each other at high enough temperature under pressure. Benzene, for example, becomes totally miscible with water at temperatures and pressures above 570 K and 200 bar [1-2]. Such a wide range variation of solubility as a function of temperature and pressure will be useful to a study of solubility phenomena on the basis of solute-solvent intermolecular interactions.

The water-hydrocarbon mixtures at high temperatures and pressures are also important in a wide range of industry including petrochemical plants, and environment-protecting technology where hydrothermal reactions are applied to destruction of toxic waste chemicals [3-7]. To understand and design those industrial processes, thermodynamic properties of the mixtures are indispensable and have been widely studied [8-15]. However, a molecular level structure of the mixtures remains largely unknown.

In addition, mutual solubility data at high temperatures and pressures are scarce. Even for the water-benzene mixture, which has been most intensively studied so far, only a limited number of data have been reported to our knowledge [16]. This is due to difficulty in measuring mutual solubility at high temperatures and pressures, which is usually carried out by sampling a small amount of mixtures and analyzing the composition with a gas chromatography or Karl-Fisher titration. The sampling without disturbing equilibrium is difficult particularly at high temperature and pressure [17].

In addition, density measurements at high temperatures and pressures put another difficulty, and the solubility data are usually given by molar fractions. However, the densities of components in the equilibrated phases are important to understand the chemical-physical properties of the mixtures on the basis of the intermolecular interactions.

Recently, we have tried to avoid those experimental problems by spectroscopic in situ measurements of the components in the high temperature-pressure mixtures. In the previous paper, the infrared spectra of water in water-hydrocarbon mixtures were measured at temperatures in the 373-533 K range and at 100 bar [18,19]. We have found that the OH stretching band intensity, as a measure of water concentration, increases remarkably with increasing temperature, and the observed bands consist of at least two components, which are assigned to monomeric and dimeric water molecules, respectively. The intensity ratio of the latter to the former increases with increasing temperature. This fact indicates that the rate of increase in water solubility with increasing temperature is larger than the rate of decrease in the equilibrium constant for the water-water association due to the entropy effect. In contrast to the remarkable temperature effects, it remains unclear how the pressure has an effect on the water solubility. In order to elucidate the pressure effect as well as the temperature effect, the present paper deals with infrared measurements of a water-benzene mixture at the extended range of temperature and pressure up to 648 K and 350 bar.

2. Experimental Method

A high-pressure cell used is schematically shown in Fig. 1. The cell body is made of nimonic alloy 80A (anticorrosion Ni-Cr alloy). An electric tape heater (EH) is used to heat the cell. Temperature and pressure of a sample fluid were measured with a thermocouple and a semiconductor strain gauge, respectively. The windows (W) of

the cell are colorless sapphire cylinders of 10 mm diameter and 8 mm thickness and the effective aperture for the optical transmission is 6 mm. The optical path length is fixed at 1 mm. A syringe pump for liquid chromatography was used for transmitting compressed liquid benzene into the cell in which a certain amount of water specimen had been put in advance and its level adjusted so as to be slightly below the optical path. The water specimen was a mixture of H_2O and D_2O with a ratio of 1:20. The ratio of the isotopic species H_2O , HDO , and D_2O in this mixture is estimated to be 1:40:400. Therefore, contribution of H_2O to the infrared OH stretching absorption can be approximately neglected as compared with that of HDO , and the observed OH band is assigned only to HDO to a good approximation. Thus we can avoid the complication of spectra due to overlap of the symmetric and antisymmetric stretching bands, which are difficult to separate and to analyze their band shapes. Another important reason for using the isotopic mixture is to obtain suitable reference spectra for extracting absorbance of water from observed spectra as described below. Spectroscopic grade benzene purchased from Nacalai Tesque (Japan) and deuterium oxide (99.9% D) from CEA (France) were used as received.

Infrared absorption of the benzene-rich phase was observed with a BOMEM DA3 Fourier-transform spectrometer. The spectral measurements were performed with 2-cm^{-1} resolution at sample temperatures in the 473-648 K range and pressures in the 100-350 bar ranges. Each of the experimental temperature-pressure points was attained at a slow enough rate, and the phase equilibration of the mixture was confirmed by the spectrum that was unchanged for at least an hour.

Absorbance of HDO in the OH stretching region was obtained by subtracting the spectrum of D_2O -saturated benzene. This is to completely cancel the absorption of benzene in the 3600 to 3700 cm^{-1} region, which changes in shape by interaction with dissolved water, particularly at temperatures higher than 530 K where water solubility in benzene is significantly large. The resulting spectra are represented by absorption

coefficients, $\alpha(\nu) = 1/(\chi_{\text{HDO}} l) \ln[I_0(\nu)/I(\nu)]$, where χ_{HDO} denotes the molar fraction of HDO in the water specimen, $l = 0.1$ cm is the optical path length, and $I_0(\nu)$ and $I(\nu)$ are the transmission intensities of the reference and the sample, respectively.

3. Results

Figure 2 shows observed spectra at 523 K (a) and 648 K (b) at a few pressures. It should be noted that the pressure effect is very small at 523 K while it is remarkable at 648 K. The integrated intensities of the absorption bands are estimated by

$$A_{\text{OH}} = \int_{\text{band}} \alpha(\nu) d\nu,$$

and plotted against pressure in Fig. 3. It is seen that the intensities at the lower temperatures, 473 and 523 K, are almost independent of pressure, while the intensities at the higher temperatures show remarkable pressure-dependent change. The slope of the intensity against the pressure is the steepest at 548 K and 100 bar and becomes less steep as the temperature rises higher. Moreover, the intensities seem to become constant at high enough pressure at constant temperatures. In addition, at constant pressures, the intensities reach maximum at a certain temperature and then decrease at higher temperatures. This fact indicates that the infrared absorption intensity, as a measure of water concentration in the mixture, exhibits a turning point when the temperature increases at constant pressure. These temperature and pressure dependencies of the intensity will be discussed by referring to the phase diagram of the water-benzene mixture in the next section.

It is worth while to mention assignments of band components seen in the spectra at 523 K. The peak at about 3648 cm^{-1} is assigned to hydrogen-bond-free OH groups while the shoulder at around 3580 cm^{-1} is assigned to hydrogen-bonded OH groups [18].

A small bulge at around 3800 cm^{-1} is a rotational side-band of the 3648 cm^{-1} band. On the other hand, spectra at 648 K show meager structure in which the two bands seem to coalesce into a single band. This point will be discussed later.

4. Discussion

As seen in Fig. 3, the infrared intensities at the lower temperatures, 473 and 523 K, are almost independent of pressure. On the contrary, the intensities at the higher temperatures increase remarkably with increasing pressure and then become constant at the higher pressures. Since the intensities are proportional to water concentrations, the plots in Fig. 3 represent effect of temperature and pressure on the water concentration in the benzene-rich phase and in the homogeneous phase. Therefore, at the lower temperatures, the water concentration is almost independent of pressure, while at the higher temperatures the water concentration depends significantly on the pressure. Fig. 4 shows plots of the intensities against temperature at some pressures. As the temperature increases at constant pressure, the intensity initially increases to a certain value and then steeply decreases at the higher temperatures. This fact indicates that the water concentration in the benzene-rich phase has a turning point. It is seen that the turning points move to higher temperatures as the pressure increases. These temperature-pressure dependencies of the intensities, or the water concentrations, may be properly understood by a phase behavior of the water-benzene mixture. Fig. 5 shows a phase diagram drawn by using literature data [2,4]. It is seen that all the experimental points at 473 and 523 K are in the two-phase region and well above the liquid-liquid-gas three-phase equilibrium line. The present experimental result that the water concentration in this region is almost independent of pressure suggests that the density of the mixture changes little along the vertical line in the phase diagram at least in the 100-350 bar range.

The temperatures of the turning points have been estimated by interpolation and the results are shown by filled circles connected with a dotted line in Fig. 5. It is interesting that the dotted line can be smoothly linked to the three-phase equilibrium curve and overlaps with the one-phase critical curve at higher pressures. This fact suggests that the density of the mixture steeply decreases around the dotted line as the temperature increases at constant pressures. The density of the mixture must jump up to a certain extent when crossing the three-phase equilibrium curve. This density discontinuity will probably show some aftereffect in the two-phase region near the three-phase end point, and causes more or less steep but continuous change in the density. This aftereffect is thought to be appreciable in the region near an extended line of the three-phase equilibrium curve. In addition, the aftereffect will decay as the temperature goes up away from the three-phase end point, and consequently the increasing rate of the density will decrease. This is consistent with the results shown in Figs. 3 and 4. As seen in Fig. 3, the pressure dependent change of the intensity is the steepest at the point of 548 K and 100 bar, which is the closest to the end point of the three-phase line as seen in Fig. 5. At the higher temperatures and pressures, the increasing rate of the intensity becomes slower as seen in Fig. 3. Therefore, the present experimental results for the effect of temperature and pressure on the infrared intensities or the water concentrations can be reasonably explained by the temperature and pressure dependent change of the density in the benzene-rich phase and in the homogeneous phase of the water-benzene mixture.

It is intriguing that the band profile becomes more symmetric as the temperature increases as shown in Fig. 6. At the lower temperatures, 473 and 523 K, the bands are obviously composed of a relatively sharp peak at about 3648 cm^{-1} and a shoulder at around 3580 cm^{-1} , and indicate coexistence of the hydrogen-bond-free state and the hydrogen-bonded state for the OH groups. In the previous study, we analyzed the band shapes at temperatures in the 373-533 K range and found that relative ratio of the hydrogen-bonded species to the hydrogen-bond-free species increases with increasing

temperature [18]. This fact indicates that the rate of increase in solubility of water with increasing temperature is larger than the rate of decrease in the equilibrium constant for the water-water association due to an entropy effect.

The band profiles at the higher temperatures, 623 K and 648 K, seem to be structureless and more symmetric as compared to those at the lower temperatures mentioned above. It seems difficult to decompose the bands into two components. Instead, the two component bands seem to merge into a single band as the temperature increases. This fact suggests that the distinction between the hydrogen-bonded and hydrogen-bond-free states become meaningless at the higher temperatures. As the temperature rises, rotational energy of a water molecule increases and, above a certain temperature, it will become enough to cleavage hydrogen bonds within a hydrogen-bonded cluster. Although the hydrogen bond energy of water, about 20 kJ mol^{-1} , is much larger than the average thermal energy at the present temperature range, 5.4 kJ mol^{-1} at 648 K, the energy barrier for molecular rotation within a hydrogen-bonded cluster may be comparable to the thermal energy. For example, the energy barrier for a hydrogen-bonded water dimer is estimated to be about 6 kJ mol^{-1} from results of the *ab initio* calculations by Matsuoka et al. [20], assuming that the bifurcated structure is a transition state as shown in Fig. 7. A hydrogen-bonded OH of the G configuration at the left can transfer to a hydrogen-bond-free OH of the G' configuration by jumping over the T configuration. Therefore, at high enough temperature, the water molecules rotate rather freely even in the hydrogen-bonded cluster. Consequently, interchange between the hydrogen-bonded and hydrogen-bond-free states of the OH groups becomes rapid enough to cause the coalescence of the two bands. This is the same in principle to the well-known phenomenon called signal coalescence due to chemical exchange in the NMR spectra. The rotational life-time of the hydrogen bonds in the water cluster is inversely proportional to the exchange rate of the two OH states. The upper limit of the life-time to yield the band coalescence can be estimated by frequency difference

between the two bands. It is estimated to be about 2×10^{-13} sec by using the wave numbers of the two bands, 3648 and 3580 cm^{-1} .

5. Conclusion

The infrared OH stretching band intensity of water in the water-benzene mixture has been obtained as a measure of water concentration in the 473-648 K and 100-350 bar ranges. In the temperature range of 473-523 K, the intensity is almost independent of pressure. On the contrary, at higher temperatures, the absorption intensities exhibit remarkable pressure dependence. The intensities increase with increasing temperature toward a certain temperature and then steeply decrease at higher temperatures. The turning points of the intensities are found to be located at an extended line of the liquid-liquid-gas three-phase equilibrium curve of the water-benzene mixture and near the critical curve between the two-phase and one-phase regions. It is suggested that density of the mixture changes steeply across those lines. From the observed coalescence of the two bands, which are assigned to hydrogen-bonded and hydrogen-bond-free OH, respectively, the rotational life-time of the hydrogen bonds in the hydrogen-bonded water cluster was discussed, and its upper limit to yield the band coalescence was estimated to be about 2×10^{-13} sec.

6. List of symbols

A_{OH}	integrated intensity of an infrared OH stretching band
I	infrared transmission intensity of a sample
I_0	infrared transmission intensity of a reference
l	optical path length of a sample

6.1. *Greek symbols*

α	absorption coefficient
χ_{HDO}	molar fraction of HDO in an isotopic mixture of water
ν	wave number

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Figure Captions

- Fig. 1 Schematics of the high pressure cell. EH: electric heater, W: sapphire windows.
- Fig. 2 Infrared absorption bands of HDO in the water-benzene mixture at a few pressures at 523 K (a) and 648 K (b).
- Fig. 3 Plots of integrated intensities of the OH stretching bands of HDO in the water-benzene mixture against pressure at various temperatures.
- Fig. 4 Plots of integrated intensities of the OH stretching bands of HDO in the water-benzene mixture against temperature at a few pressures.
- Fig. 5 Pressure-temperature phase diagram for the water-benzene mixture.
Thick solid lines: one-phase critical curve and liquid-liquid-gas three-phase equilibrium curve; closed circle: turning points of the intensities; c.p.: critical point.
- Fig. 6 Comparison of the band shapes at some temperatures at 350 bar. Each spectrum is normalized at the peak maximum.
- Fig. 7 Schematics of an exchange mechanism between the hydrogen-bonded and the hydrogen-bond-free OH of HDO within a water dimer (a) and a potential energy curve for the rotational jump (b).

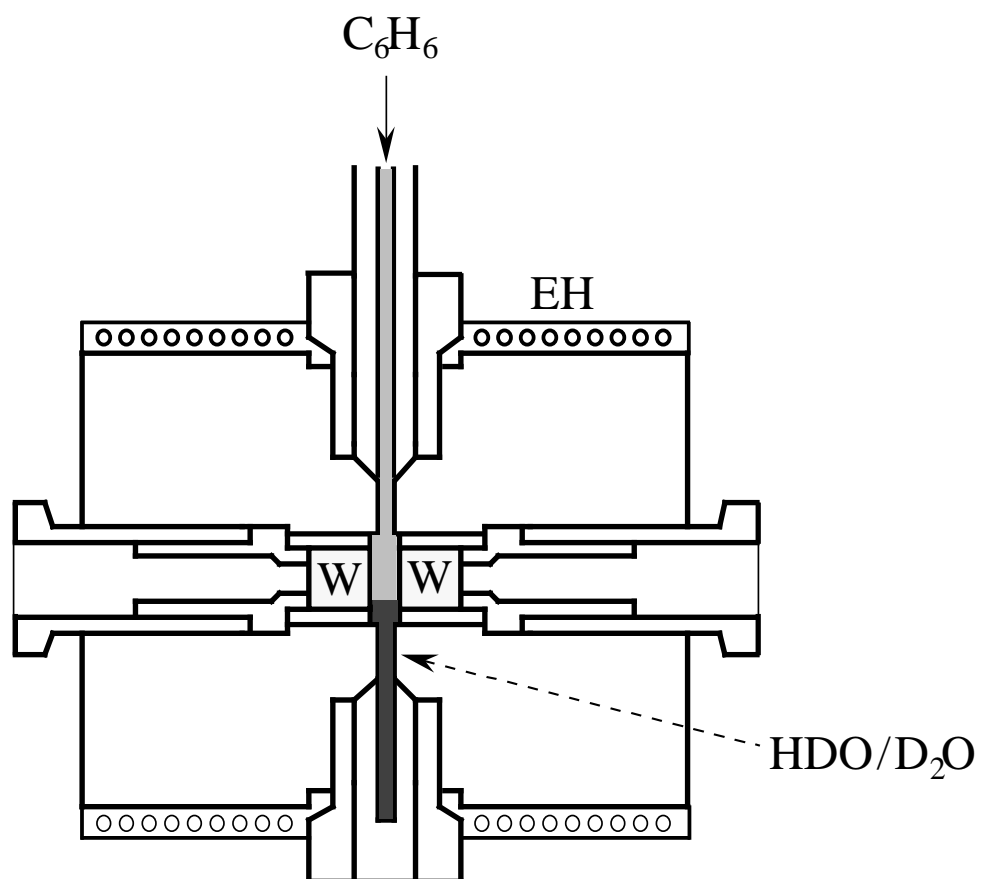


Fig. 1 Furutaka & Ikawa

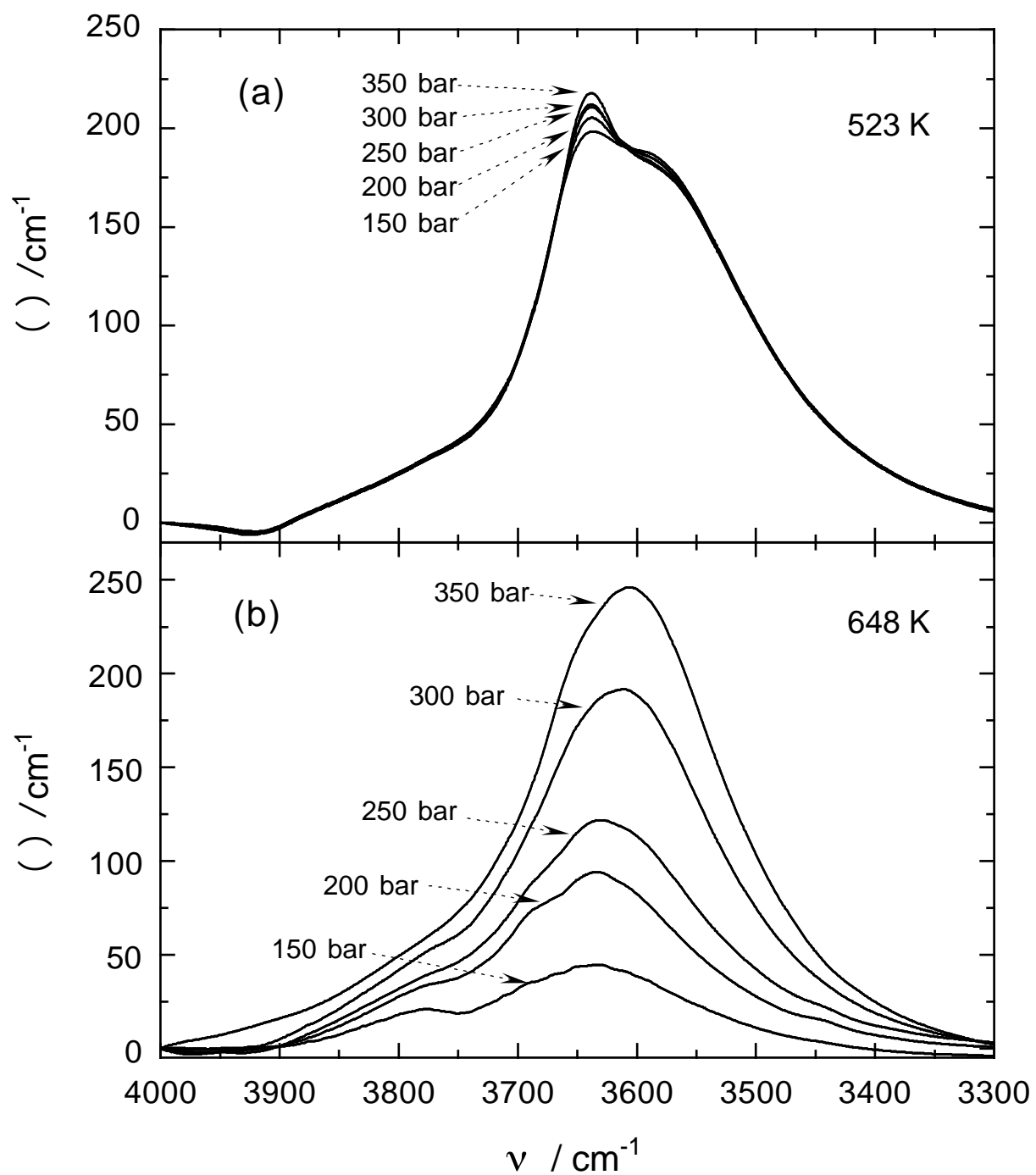


Fig. 2 Furutaka & Ikawa

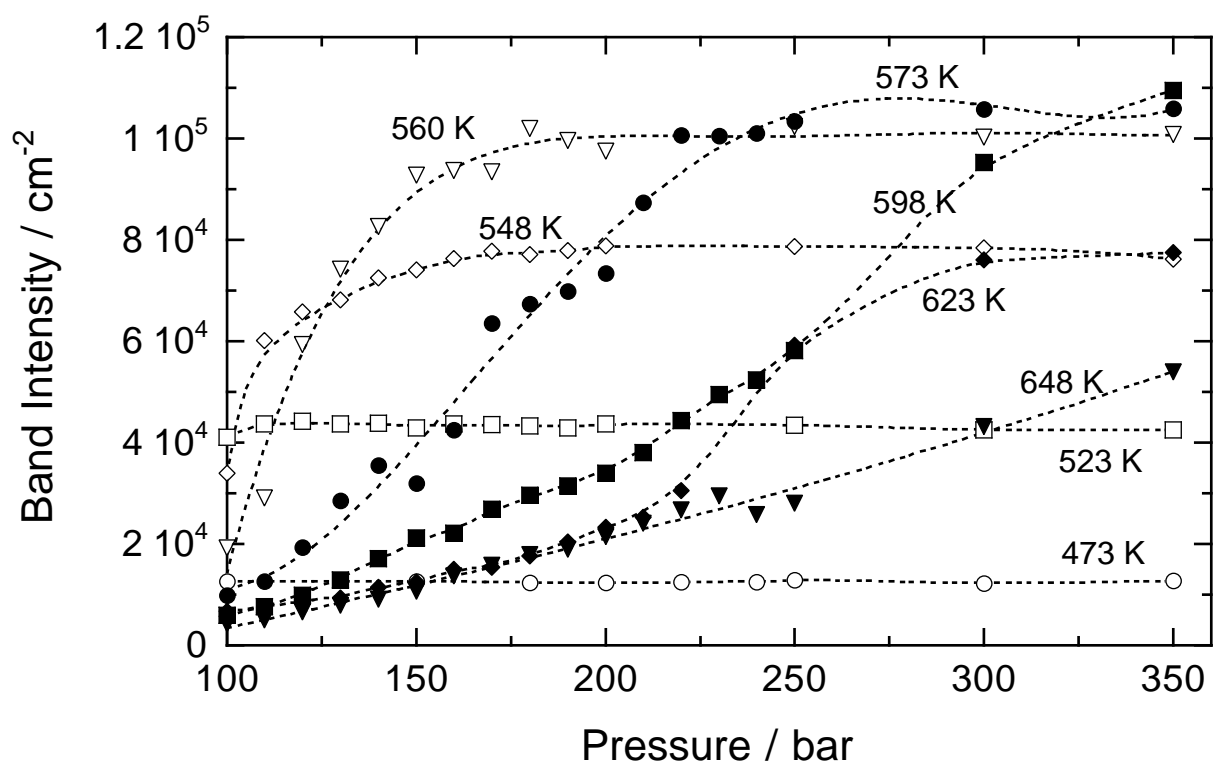


Fig. 3 Furutaka & Ikawa

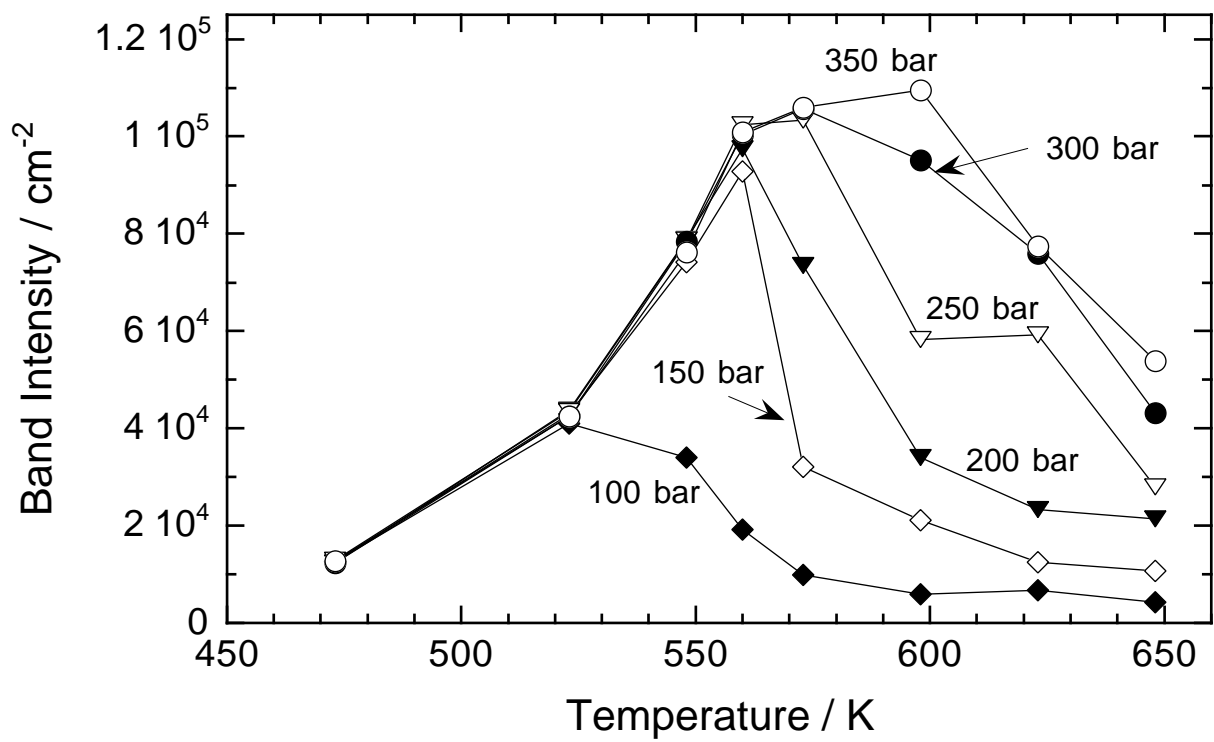


Fig. 4 Furutaka & Ikawa

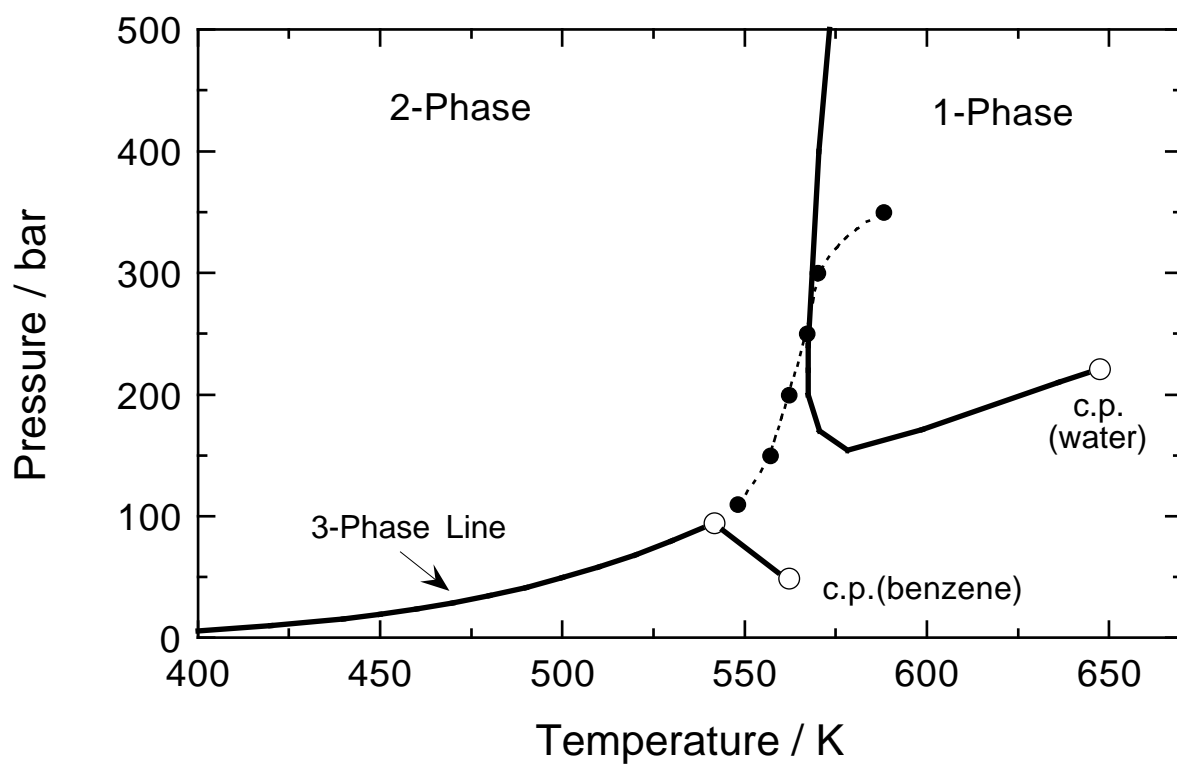


Fig. 5 Furutaka & Ikawa

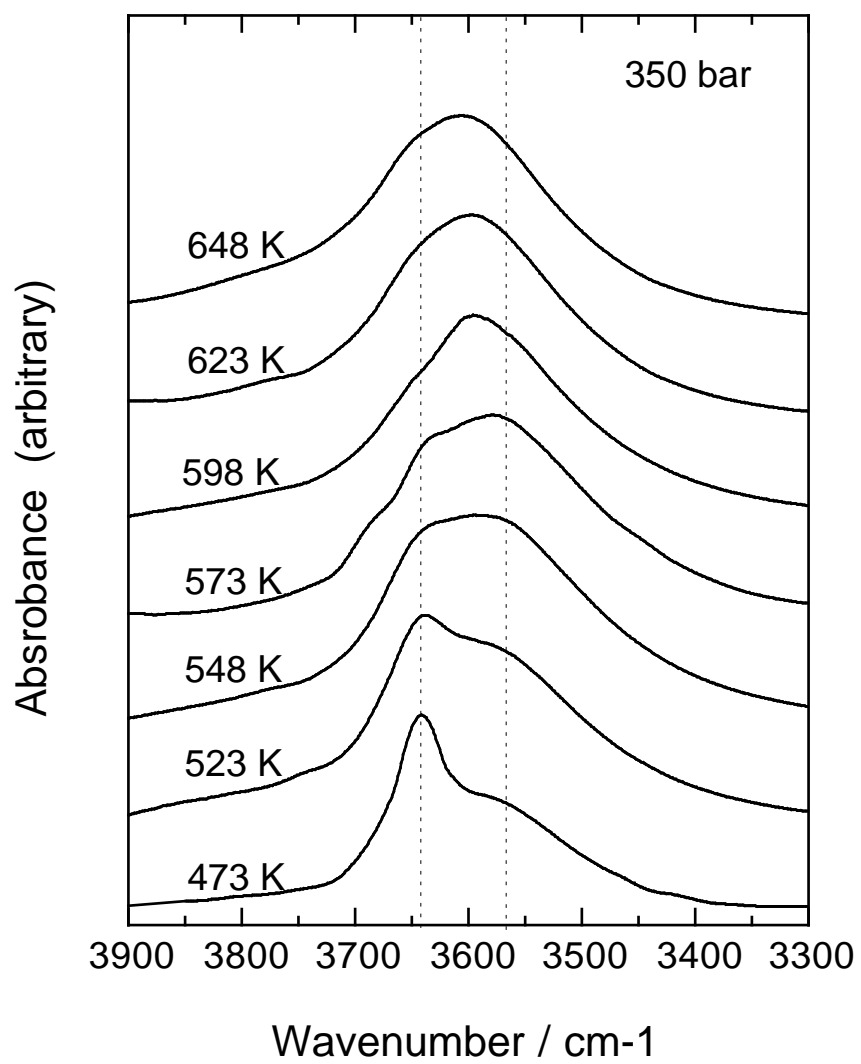


Fig. 6 Furutaka & Ikawa

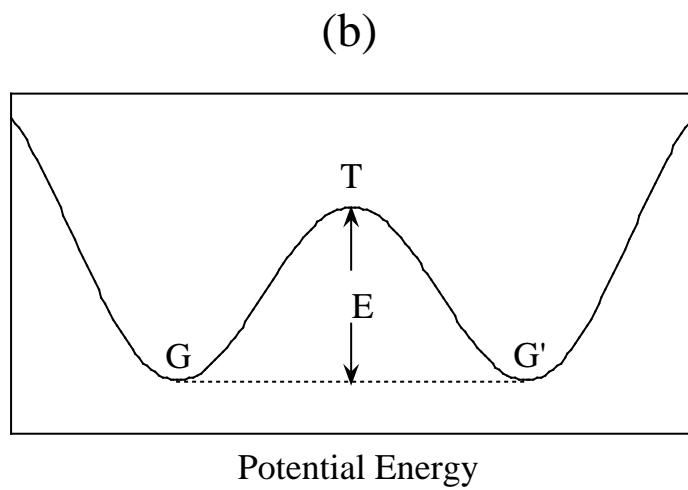
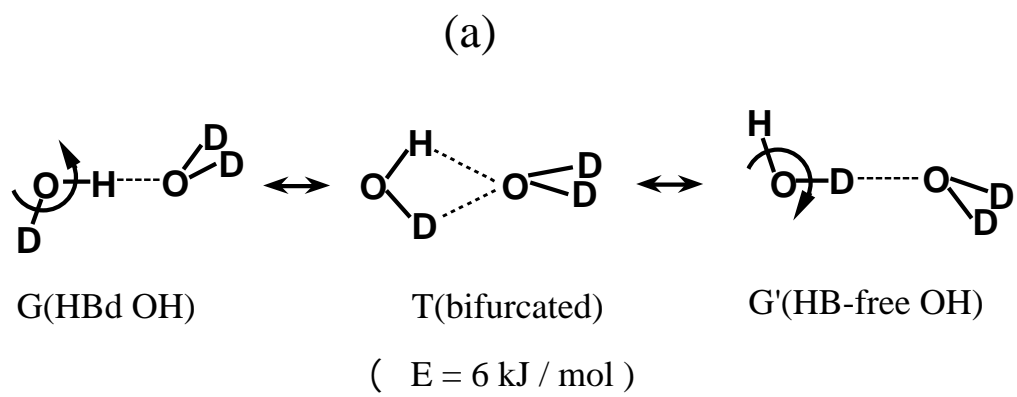


Fig. 7 Furutaka & Ikawa